

Heavy Metals in Agricultural Lands
Receiving Chemical Sewage Sludges
Volume III

Research Report No. 30

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**Research Program for the Abatement of Municipal Pollution
under Provisions of the Canada-Ontario Agreement
on Great Lakes Water Quality**

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These RESEARCH REPORTS describe the results of investigations funded under the Research Program for the Abatement of Municipal Pollution within the provisions of the Canada-Ontario Agreement on Great Lakes Water Quality. They provide a central source of information on the studies carried out in this program through in-house projects by both Environment Canada and the Ontario Ministry of the Environment, and contracts with municipalities, research institutions and industrial organizations.

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HEAVY METALS IN AGRICULTURAL LANDS
RECEIVING CHEMICAL SEWAGE SLUDGES

VOLUME III

by

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RESEARCH PROGRAM FOR THE ABATEMENT
OF MUNICIPAL POLLUTION WITHIN THE
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ABSTRACT

This report describes existing and newly developed methods for the analysis of metals in sewage sludges. Atomic absorption and electrochemical techniques are emphasized. Procedures developed specifically for arsenic, selenium, mercury, tin and molybdenum analyses are included.

The quartz "T" tube furnace for flameless atomic absorption studies of thermal volatility and gas chromatography of metal compounds in sludge has been developed and is described.

A number of chemical sewage sludges were analysed for metals and the results are tabulated.

RESUME

Le présent rapport traite des méthodes établies et nouvelles de dosage des métaux dans les boues des eaux résiduaires. L'absorption atomique et les méthodes électrochimiques y occupent une place importante, et on y trouvera des méthodes spécifiques à l'arsenic, au sélénium, au mercure, à l'étain et au molybdène.

Le four à tube de quartz en forme de T pour l'absorption atomique sans flamme, appliquée à l'étude de la volatilité et en chromatographie en phase gazeuse des composés métalliques présents dans les boues a été perfectionné et le présent rapport en traite.

On a fait l'analyse d'un certain nombre de boues chimiques et les résultats sont présentés sous forme de tableaux.

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1. INTRODUCTION

This study was divided into two subject areas:

A. Analytical Methods Development for Metals

B. Sludge Analysis for Metals

In category A, work was centred on atomic absorption and electrochemical (anodic stripping and polarographic) methods. Methods development work is still focusing on "total" metal analysis because of a lack of proven procedures for such important elements as As, Se, Mo, etc. Procedures developed for these elements are included.

There has been an interest in evaluating the potential of electrochemical techniques, particularly polarography and anodic stripping, for sludge analysis. These techniques were investigated in this study; results and preliminary conclusions follow.

In the future, in category A, flameless atomic absorption will be evaluated for the analysis of sludge. This technique may have an important application in the determination of total metals which are difficult to analyse by flame methods (e.g. see Mo procedure below). However, flameless atomic absorption is presently being investigated as a possible method of identifying the forms of metals which occur in sludge. In this regard, a quartz "T" tube furnace has been developed which can be used for thermal volatility studies and gas chromatographic studies of metal compounds in sludges. As a spin-off benefit of this study, data will be obtained for potential metal losses to stack gases due to incineration, if this method is used for sludge disposal. Early results of this investigation are included in this report.

In category B, available chemical sludges are being routinely analysed for metals. A tabulation of results from four new plants is included in Section 7 of this report.

2. ANALYTICAL METHODS FOR ARSENIC, SELENIUM, MERCURY, TIN AND MOLYBDENUM

2.1 Provisional Method for Determining Arsenic and Selenium in Sludge

Difficulties are experienced in the atomic absorption determination of As and Se because the best resonance lines are in the Uv at 1937Å and 1960Å, respectively. At these wavelengths much of the incident radiation from the source is absorbed by air and flame gases. Hence, sensitivities, if aspirating aqueous solutions of these elements into flames, will be poor.

A number of authors, e.g. (1-7) recommended the production of As and Se hydrides as an improved method of introducing these elements into the atomizer (flame or flameless). This method minimizes interference problems from the matrix and atomization efficiency is increased. In this study, based on past experience, it was assumed that a flameless atomizer would also improve the detection limit.

The following describes a very simple method of hydride generation involving only a 50¢ syringe. This can replace the commonly used apparatus, which is complex, time consuming and expensive. A method is described which utilizes the syringe in conjunction with an electrically heated, home made, quartz "T" tube furnace.

2.1.1 Decomposition methods As, Se

There is a danger that these elements will be lost during decomposition. This possibility is greatest if chlorides are present or if reducing conditions occur. Work to date suggests that a nitric acid/sulphuric acid or nitric acid/perchloric acid mixture would be useful for most of the sludges. If a 100% recovery is required, the safest procedure seems to be a fusion of the sample with a KOH and Na₂O₂ mixture. More work is required before making a final recommendation on sample decomposition.

2.1.2 Apparatus and reagents

The method was tested on both Jarrel Ash 810 and a Perkin Elmer 305B atomic absorption spectrophotometer. For flameless work, a heated quartz cell similar to that described by Vijan and Wood (6) was used.

The analytical lines and slit width were 1937Å, 1Å, and 1960Å, 1Å for As and Se, respectively.

Standard 1000 ppm As and Se solutions were prepared by acid decomposition of pure metals. Final acid content of a 1000 ml solution was a 100 ml concentration H_2SO_4 and a 50 ml concentration HNO_3 . Dilute working solutions of 1, 5, 10, 50, 100, 250 and 400 ppb were prepared fresh weekly by dilution of a 1 ppm intermediate mixed As, Se standard solution. An appropriate aliquot was placed in a 1000 ml flask together with 100 ml concentrated H_2SO_4 and 50 ml concentrated HNO_3 and diluted to the mark with water.

Disposable syringes were 50 cc plastipak R-1314 B-D, fitted with plastic top #18 stainless steel needles. Each syringe can be used at least 100 times.

The recommended reductant is a 1% solution of sodium borohydride prepared by dissolving the required amount of the salt in 100 ml of water containing one pellet of KOH.

2.1.3 Atomic absorption procedure

The quartz absorption cell is connected to the gas cylinders by a glass "Y" tube and soft plastic tubing. Gas flows are adjusted to maximize signal without yielding prolonged memory effects (see below). The quartz tube is used at about 800°C. Automatic background correction is recommended. Gas flows, lamp outputs and cell temperature are allowed to equilibrate for 5 minutes.

The needle of the syringe is inserted into a standard or sample solution with the syringe plunger firmly depressed. (Sample must be cool-room temperature.) Five cc of solution is extracted. Any drops are wiped from the needle. The needle is inserted into the borohydride solution and the plunger is withdrawn to the upper black line (2 oz mark). Only a small quantity of borohydride is consumed and most of the space is occupied by gases. The syringe is inverted quickly. Any liquid expelled from needle tip is wiped away. With the syringe inverted, the needle is inserted through the plastic tubing at a point about 3 inches from the inlet to the absorption cell. The instrument is adjusted to zero.

The integration button is pressed and set at 2 second integration. The plunger of the syringe is depressed immediately. Injection is stopped just prior to the liquid reaching the needle. The injection period should end just prior to the expiry of the 2 second integration period. This step requires some practice but acceptable reproducibility can be obtained after a short time. Blanks must also be run.

2.1.4 Choice of purge gas

Argon has been used by most workers to purge the atomization cell. Nitrogen is much cheaper and would be preferable if its use was acceptable. Table 1 shows a comparison of typical absorbance obtained in nitrogen and argon purged atmospheres.

TABLE 1. COMPARISON OF PURGE GASES.

	N ₂	Ar
As (5 ppb)	.070	.090
Se (50 ppb)	.060	.102

While there is a definite suppression with nitrogen, unless the best sensitivity is required, nitrogen can be used.

2.1.5 Interferences

The effects of some common major matrix constituents were studied directly. No interference was found for up to 1000 ppm of Na, K, Mg, Ca, Fe⁺³ and Al. Further evidence for lack of interference was obtained by analysing complex standard reference samples (see results below). Values obtained agree reasonably with accepted values, indicating minimal interferences in these sample types. While little problem was noted in these cases, it is important to investigate interference problems if samples of much different composition to the above are to be run. For example, in an unrelated work (metallurgical) the author found a large suppression of the As signal in the presence of 10,000 ppm Cd.

Recent work suggests that some organic materials may suppress release or production of the hydrides and, therefore, it is important to destroy these compounds during sample preparation. If complete destruction of organics cannot be assured, it has been shown that the addition of an organic material, such as gelatin, to the standards in small amounts will compensate for this problem.

2.1.6 Gas flow rate adjustments

When excessive purge gas flow rates are used, the absorption signals are unnecessarily small due to the quick removal of analyte atoms from the optical beam. If the purge gas flow rate is too slow, analyte atoms will remain in the optical beam for excessive periods of time, resulting in a memory effect for many seconds after the integration reading has been taken. It is important to experiment with the purge gas flow rate velocity through the cell to find a condition which gives suitable signals during atomization but minimizes the memory effect. In the author's experience, conditions should be such that the signal returns to zero within about 10 seconds after atomization has been initiated.

Hydrogen flow rate should be such that a very small flame appears at the end of the quartz tube.

Another advantage of the proposed method over others is the relatively slow flow rate of gases required. It was found that the very modest rate of about 0.5 litres per minute of each gas gave optimum results.

It is not sufficient to use argon as a inert purge gas alone. If only an inert gas is used, a memory effect occurs, particularly with selenium, due to deposition of metals on cooler parts of the cell. The introduction of a constant slow flow of hydrogen results in a hydrogen diffusion flame and a continual flushing of the cell.

2.1.7 Results

The above procedure was tested on a variety of "standards". Table 2 gives the results, compared with accepted values of the standards.

TABLE 2. ARSENIC AND SELENIUM ANALYSIS (ppm).

	As			Se		
	$\bar{x}$	Sx	Ac	$\bar{x}$	Sx	Ac
NBS Orchard Leaves SRM 1571	8.6	± 0.3	11	0.10	± 0.02	0.08
NBS Bovine Liver	0.06	± 0.01	0.06	1.2	± 0.0	1.1
NBS Flyash	55	± 6	61	-	-	9.3
Kodak Gelatine TEG 50-A	41	± 1	41*	48	± 3	43*

* Neutron activation used because insufficient data were available for these elements to yield an accepted value.

Ac - Accepted values

These results are in acceptable agreement with values quoted. Sludges were analysed by this procedure and the results are given in Section 7.

With a 4 inch quartz cell, the solid sample detection limits are 10 ppb Se and 2 ppb As.

2.1.8 Linearity of calibration curve

Using the 4 inch quartz cell, operated according to the proposed procedure, linearity is obtained up to 100 ppb for As and 250 ppb for Se.

2.1.9 Conclusions

The proposed procedure yields somewhat poorer precision and poorer sample detection limits than some of the conventional hydride, atomic absorption methods.

The following advantages can be stated:

- 1) Samples can be processed at the rate of one every 40 seconds. (Compared to several minutes with conventional methods.)
- 2) The apparatus is inexpensive and readily assembled in most laboratories from existing supplies.
- 3) The technique can be used with most existing atomic absorption equipment with great simplicity.

Although early results using this procedure are encouraging, workers are cautioned that more extensive testing of interferences is necessary before it can be recommended for routine work. Testing is being carried out and results will be recorded in Volume IV for this research project.

2.2 Provisional Method for Mercury Analysis in Sludge

It was evident from an early stage in the arsenic and selenium work that such a system might be applicable to mercury analysis. A number of authors have recommended modifications of the extremely useful Hatch and Ott method. Most of these proposals use a pump for mercury injection into a cold vapour absorption tube. The present proposal eliminates the need for recirculating pumps and allows easy conversion of conventional atomic absorption equipment for mercury analysis.

The method proposed below uses a modified Hatch and Ott sample decomposition procedure. Instead of the stannous chloride reductant a solution of sodium borohydride is used. Acid solutions containing mercury react vigorously with sodium borohydride, yielding hydrogen gas and mercury vapour. The hydrogen gas, vigorously bubbling through the sample solution in the syringe, volatilizes the mercury into the space above the solution. Inverting the syringe sends the solution against the piston of the syringe and allows free passage of the mercury containing gases out through the needle. The complete reaction and gas injection process takes about 40 seconds.

2.2.1 Apparatus and reagents

The method was tested in a number of atomic absorption units, e.g. Jarrel Ash 810, Perkin Elmer 305B, 303 and Instrumentation Laboratories 153. The 2536 Å Hg line and a slit of 7 Å were used. Best results were obtained with equipment using automated background correction. The cold vapour absorption cell was obtained from Coleman Instruments (replacement part for MAS-50).

A standard 1000 ppm mercury solution was prepared by dissolving the metal in nitric acid. Dilute working solutions were prepared weekly to contain 10% final acid concentration. The acid composition of these solutions was 2/3 nitric, 1/3 sulphuric. Blanks must be used.

Disposable syringes were 50 cc plastipak R-1314 fitted with 3 inch #18 needles, stainless steel with plastic fittings. Each syringe can be used at least 100 times.

The reductant is prepared by dissolving 1 gram of sodium borohydride in 100 ml of water containing one pellet of potassium hydroxide.

2.2.2 Recommended procedure

The absorption tube is centred in the optical path as recommended below. The air flow rate through the cell is adjusted to give maximum signal but no appreciable memory effect, as indicated below. The background corrector is turned on and the signals from this device and from the hollow cathode are properly balanced. The system is allowed to equilibrate for 15 minutes.

With the syringe plunger firmly depressed, the needle of the syringe is inserted into a standard or sample solution. (Sample must be cool-room temperature.) Five cc of solution is extracted. Any drops are wiped from the needle. The needle is inserted into the borohydride solution and the plunger is withdrawn to the upper black line (2 oz mark). Only a small quantity of borohydride is consumed and most of the space is occupied by gases. The syringe is inverted quickly. Any liquid expelled from needle tip is wiped away. With the syringe inverted, the needle is inserted through the plastic tubing at a point about 3 inches from the inlet to the absorption cell. The instrument is adjusted to zero and the integrated button is set at a 2 second integration. The plunger of the syringe is depressed immediately. Injection is stopped just prior to the liquid reaching the needle. The injection period should end just prior to the expiry of the 2 second integration period. This step requires some practice but acceptable reproducibility can be obtained after a short time. Blanks must also be run.

2.2.3 Centering of absorption tube

The most convenient method of adjusting the position of the absorption tube is through use of the burner horizontal and vertical adjustments. Hence, it is advisable to mount the absorption tube in the burner mount at a position where the burner adjustment controls can

conveniently centre the tube in the optical path. Once this mounting has been established, the tube can be centred as follows.

The Hg lamp is turned on and the vertical and horizontal burner controls are adjusted until a minimum absorbance is indicated on the instrument readout. Some slight readjustment may be necessary when the background correction is turned on.

2.2.4 Air flow rate adjustment

When excessive air flow rates are used, the mercury signals are unnecessarily small due to the quick removal of mercury atoms from the optical beam. If the air flow rate is too slow, mercury atoms will remain in the optical beam for excessive periods of time, resulting in a memory effect for many seconds after the integration reading has been taken. It is important to experiment with the air flow rate velocity through the cell to find a condition which gives suitable signals during atomization but minimizes the memory effect. In the author's experience, conditions should be such that the signal returns to zero within about 10 seconds after atomization has been initiated.

2.2.5 Need for background corrector

One of the weakest points of much of the equipment commercially available for mercury analysis is lack of background correction capability. To compensate for this lack, many workers have used vapour (particularly water) absorption tubes. In the author's experience, these tubes trap some mercury. Background correction provides an easy method for eliminating absorption effects due to molecular species.

In the case of the present procedure, H_2 , AsH_3 etc. gases are produced along with the mercury. Therefore, it is essential to employ background correction to guard against potential problems from these species.

One of the important advantages of the proposed procedure is its ready application to existing atomic absorption equipment, much of which has background correction capability.

2.2.6 Choice of reducing agent

Sodium borohydride reacts with acid solutions, producing H_2 gas, and reduces many other species in solution. In the case of the presently proposed procedure, mercury present in many forms is reduced to mercury metal. This simultaneous, vigorous generation of H_2 gas sweeps the metallic mercury into the gas phase in the syringe. Sodium borohydride was found to be the most convenient and most efficient reagent for this purpose.

2.2.7 Temperature of absorption tubes

The proposed procedure was tested with both heated and cold absorption tubes. Since mercury had been atomized in the syringe, little difference in absorption values was expected. Results show that slightly lower results were obtained in hot tubes.

2.2.8 Open vs closed tubes

Substantially higher values were obtained using close ended absorption tubes. The commercially available tube used in the Coleman MAS-50 unit was found to be conveniently applicable to the proposed procedure. Home-made tubes can also be used.

2.2.9 Subjectivity of the syringe technique

Beyond any question, there is an element of subjectivity in using the proposed procedure. However, employing short integration times and with some practice, reproducibility of $\pm 20\%$ or better can be achieved. If the syringe becomes sticky (difficult to operate), it should be washed out with soap and then lubricated with silicone stop cock grease.

With highly organic sample solutions, excessive frothing during the reduction step can be a problem. After inverting the syringe, a Kleenex should be placed over the syringe tip for several seconds until frothing subsides.

2.2.10 Sample preparation

Depending on sample type and analysis requirements, a variety of sample preparation techniques can be employed. The decomposition procedures recommended by Hatch and Ott (8) or Rains and Menis (9) can

be used. However, the sample solution for analysis should be adjusted to contain 10% acid, of which preferably 2/3 should be nitric and 1/3 sulphuric.

2.2.11 Interferences

No comprehensive study of interferences was made. Presumably, the patterns are similar to those found for other cold vapour mercury procedures. However, real samples were analysed for mercury by the proposed procedure. The results obtained on standard reference materials, which contain a wide variety of matrix constituents, suggest interferences are minimal. However, more extensive testing is being carried out and results will be presented in Volume IV for this project. Therefore, this procedure is not yet recommended for routine work.

2.2.12 Range of linear response

Using the absorption tube described, linear response is obtained with solutions containing up to 100 ppb levels of mercury.

2.2.13 Results

A number of samples were analysed using the proposed procedure. Results of analyses performed on interference standards are given in Table 3.

TABLE 3. MERCURY ANALYSIS (ppm)

Sample	Hg Found	Hg Provisional
Kodak TEG Multimetall	32 ± 3	-
NBS Orchard Leaves SRM #1571	0.11 ± 0.02	0.16
CCIW Sewage Sludge "D"	7.7 ± 0.2	8.7
"F"	2.3 ± 0.2	1.7
Bovine Liver SRM #1576	0.01 ± 0.002	0.016

These results show acceptable agreement with provisional values of the standard.

2.2.14 Sensitivity and detection limits

Using the Perkin Elmer 305B and a 2 second integration time, a 20 ppb solution run according to the proposed procedure gives an absorbance of 0.14 ± 0.01 . As yet, it is not possible to give a definitive answer to the question of sensitivity and detection limits. Further experience with the technique is required.

It is clear, however, that the proposed method does not have as good a sample detection limit potential as the Hatch and Ott evolution techniques. The present procedure requires the use of a 5 ml portion of the solution, while many evolution techniques can use the total sample solution. This will not be a serious disadvantage in sludge analysis.

The proposed method is faster than conventional methods and, in addition, allows essential background correction to be done.

2.3 Tin Analysis in Sludge

Tin levels in many sludges are in the low to sub-ppm range. Conventional flame atomic absorption gives adequate detection limits for most sludges. The air hydrogen flame, although yielding better sensitivity, also results in serious chemical interference problems not found with hotter flames.

At the present time, this laboratory is evaluating a hydride evolution method for tin closely related to that described for Se and As. Initial work indicates a detection limit of 50 ppb which would make the method useful for sludge analysis. At present, interferences are being studied. Results, to date, suggest that most sludge constituents will not cause a problem. Hence, it appears likely that the hydride generation method will prove suitable for tin analysis in sludges. Further details will be presented in Volume IV for this project.

2.4 Molybdenum Analysis in Sludge

A number of authors e.g. (10-13) have recorded flame atomic absorption procedures for molybdenum. These and other studies demonstrate a wide range of chemical interference problems. Although both air-acetylene and nitrous oxide-acetylene flames have been used, the latter flame type has been shown to yield better sensitivity and a simpler

pattern of interferences. However, even with the relatively hot nitrous oxide-acetylene flame, enhancement and depressive effects of up to 90% have been recorded for some salts, e.g. CaCl_2 (14). Detection limits for Mo in aqueous sample solutions using the flame techniques are generally no better than 1 ppm.

Some workers, e.g. (15), (16) have recorded solvent extraction concentration methods for Mo for use with flame atomic absorption. Use of this additional sample preparation step allows detection of Mo to a few ppb.

Flameless atomic absorption spectroscopy has been widely publicized as a method which yields much better detection limits than flames using direct injection of aqueous sample solutions. This claim seems to hold well for simple matrix samples such as fresh water and high organic content materials. The flameless method also seems advantageous when the analyte, e.g. Hg, As, has been chemically separated in the form of a gas from a complex matrix. However, this generalized view has been challenged by Cruz and Van Loon (17) for the large variety of sample solutions which are high in relatively nonvolatile inorganic salts.

The present study has examined the usefulness of a flameless technique for determining Mo in highly organic to mixed organic/inorganic matrix samples. A Perkin Elmer graphite furnace atomizer was used. Of the commercial offerings, this device allows use of the largest sample solution volume and, therefore, offered the best potential solid sample detection limit.

Johnson et al (18) studied Mo determination using a flameless carbon filament atom reservoir. These authors used very small (1 μl) aliquots and found an optimum working calibration range of 0.1 to 10 ppm Mo. No chemical interferences were noted for 1000-fold higher levels of Na^+ , Ca^{+2} , Mn^{+2} , Mg^{+2} , Cu^{+2} , Fe^{+3} , Zn^{+2} , V^{+5} , Sn^{+2} , phosphate $\text{SO}_4^{=}$ or NO_3^- .

Henning and Jackson (19) used an HGA 70 Perkin Elmer graphite furnace to analyse Mo in plant tissue. Unfortunately, little indication is given in this paper that optimization studies were performed for critical parameters such as heating cycle times and temperatures, nature

and rate of purge gas, and possible presence of background interference problems. These authors recorded a working range of approximately 0.01 to 0.4 ppm.

2.4.1 Reagents and equipment

A Perkin Elmer HGA 2000 graphite furnace was used with a Perkin Elmer 303 atomic absorption spectrophotometer. Operating conditions are listed in Table 4.

TABLE 4. INSTRUMENT OPERATING CONDITIONS.

Wavelength,	3133 Å
Slit width,	7 Å
Heating cycle	
Dry	100°C - 60 sec.
Ash	1000°C - 40 sec.
Atomize	2700°C - 30 sec.
Purge gas, N ₂	- 2 ft ³ /h
Lamp current	- 25 ma.

Signals were recorded using a Sargent Welch, Model SRL potentiometric recorder. An Instrumentation Laboratories Mo hollow cathode lamp was used.

Acids used were Fisher ACS reagent grade. Metal solutions were prepared from reagent grade (Fisher ACS) salts or spec pure metals. These metals solutions were generally prepared to contain 0.1 - 1% acid. The 1000 ppm Mo stock solution was prepared to contain 1 N H₂SO₄.

Mo working standards were prepared fresh weekly over the range 25-500 ppb in 0.1% sulphuric acid.

Solutions were added to the furnace using a 50 µl Eppendorf pipet equipped with disposable plastic tips.

2.4.2 Proposed procedure

The following procedure has been found suitable for highly organic and mixed organic/inorganic matrices such as sewage sludge. Samples are dissolved by a suitable procedure, e.g. (17) (19).

The instrument is turned on and allowed to warm up for 20-25 minutes at the adjustments given in Table 4. Nitrogen purge of the furnace should be carried out during approximately the last 10 minutes of this period. If the furnace is newly installed or if samples high in Mo have previously been run, it should be fired for 30 seconds, 10 times at maximum temperature prior to actual use.

A 50 μ l aliquot of sample solution containing from 25 to 500 ppb Mo is placed into the furnace using the preferred technique (20) as follows:

The pipet is fully depressed (2 stops). The tip is inserted into the solution. The plunger is fully released. The pipet tip is placed into the furnace and depressed to the first stop. The pipet is removed and the tip is discarded.

The start button is depressed and the various heating stages are allowed to proceed. The recorder pen and drum are automatically activated by the HGA power supply just prior to atomization to eliminate spurious recordings prior to the appearance of the desired peak.

A suitable range of standards are run at the beginning and end of each run. If a large number of samples, (>10), are done, then standards should be run more frequently.

Standard reference materials of suitable matrix, e.g. NBS Orchard Leaves, Bovine Liver, TEG-50, etc. should be used for control purposes with each determination set.

2.4.3 Furnace heating conditions

Extensive tests were run to find optimum drying, ashing and atomization temperatures. A drying temperature of 100°C for 60 seconds was suitable for the sample solutions tested. It is important to maintain drying conditions which do not cause spattering of the sample inside of the furnace.

An ashing temperature of 1000°C minimizes matrix effects which might be experienced during atomization without inflicting detrimental effects in the analyte. Except in the case of easily volatilized matrix constituents, e.g. organics, alkali metal salts, little benefit is obtained in simplifying matrix problems during the ashing step. A tempera-

ture of 1000°C was used over a period of 40 seconds. Longer ashing times were found to give no appreciable improvement.

The refractory nature of Mo compounds requires a high atomization temperature. The maximum obtainable temperature, using PE, HGA 2000, is about 2700°C . This is not a measured temperature but is specified as obtainable by the manufacturer under the operating conditions used.

A variety of atomization times and temperatures were tested. The maximum (2700°C) temperature for 30 seconds was found to be optimum. For example, at a temperature of 2600°C the absorbance decreased by more than 50%.

Memory effects were found to be a problem even at 2700°C because of the incomplete atomization of Mo if the Mo concentration was high. A 30 second atomization time was adequate for complete atomization from samples containing up to 500 ppb Mo. This level is the highest recommended for the proposed procedure. If sample solutions above this level are inadvertently run, the furnace should be fired at maximum temperature in 30 second bursts until the residual Mo is volatilized.

2.4.4 Furnace conditioning and lifetime

To obtain maximum reproducibility with Mo, it is important to condition new furnaces at maximum temperature prior to their use. Best results are obtained if the new furnace is fired 10 times for 30 seconds at maximum temperature. The furnace can then be used 50 to 55 times before it should be replaced, because of decreased and variable absorbances.

2.4.5 Peak height vs integration

The absorbance is obtained by reading peak height (% absorption) and converting to absorbance. Peaks are somewhat broad but the peak maximum can easily be read. No significant advantage could be seen for using integration.

2.4.6 Purge gas

Much work has been done with flameless devices employing argon as a purge gas. Several authors have found the less expensive N_2 gas to

be as good as or better than argon for purging purposes. The present work with molybdenum demonstrated that the use of N_2 gas yields results comparable to those obtained with argon.

Purge gas flow rate was found to be optimum at $2 \text{ ft}^3/\text{h}$. Although lower rates gave higher absorbance, memory effects were greatly enhanced. Rates higher than $2 \text{ ft}^3/\text{h}$ caused lower absorbances because of the removal of atoms from the optical path at an excessive rate.

2.4.7 Chemical interferences

A wide range of chemical interferences have been noted in the flame atomic absorption determination of molybdenum, e.g. (11), (14), and (15). A variety of salts, particularly Al^{+3} and Ca^{+2} , cause major problems. Interferences from such salts, added in levels usually found in sample solutions, were examined. No chemical interference greater than 10% enhancement or depression was found.

2.4.8 Background (non-specific) interference

Non-flame devices commonly show very serious interferences from molecular absorption or light scattering effects. In the case of molybdenum, for the sample types tested, background correction was not found to be necessary.

2.4.9 Results

Samples were analysed for molybdenum and the results are given in Table 5.

The values obtained by the proposed procedure agree reasonably well with accepted values for the two standard samples.

It is to be expected that higher atomization temperatures will yield better absorption peaks for molybdenum. Some equipment which will soon be available from instrument manufacturers will generate temperatures over 3000°C . Molybdenum studies with this equipment must be awaited with interest.

TABLE 5. MOLYBDENUM VALUES IN SAMPLES (ppm)

Sample	Values Obtained	Accepted
TEG 50	56 $\pm$ 4	55-60
Bovine Liver	3.0 $\pm$ 0.4	3.2
Sewage Sludge - North Toronto	6 $\pm$ 0.5	-
Newmarket	0.3 $\pm$ 0.1	-
Point Edward	3 $\pm$ 0.5	-

3. USE OF LESS SENSITIVE ATOMIC ABSORPTION LINES

A number of the heavy metals, e.g. Zn, Pb, Cu, Fe and Mn are present in relatively high levels in sludges from urbanized centres. The most commonly recommended wavelengths are so sensitive that large dilutions of sludge sample solutions are required to adjust the concentration of these elements into the linear working range.

To avoid such time consuming and sometimes error-causing work, two procedures are commonly employed:

- 1) The path length of the optical beam in the flame is decreased by rotating the burner head.
- 2) A resonance absorption wavelength of lower oscillator strength is used.

Rotating the burner head can decrease the signal intensity by up to a factor of ten. Unfortunately, this procedure also results in an enhancement of the flame noise to signal ratio. In many cases, the increase in noise invalidates the use of this procedure and, therefore, it is not generally recommended.

The most sensitive absorption lines, those representing transitions from the ground state to the lowest energy excited state, usually yield the best signal to noise ratios. Hence, use of less sensitive lines (lower oscillator strengths) is likely to result in noisier readings. However, a number of researchers in related fields have recommended the use of less sensitive lines for high concentrations of some elements as a better trade-off than extensive dilutions. It is important to evaluate the results obtained for high concentration elements in sludges using less sensitive lines.

Preliminary tests were performed for all the alternative, less sensitive lines listed in Corliss and Bozmin (21). The following were then chosen for extensive analytical testing.

The deuterium arc was used for background correction, for the 3683.5 Å lead line.

Element	Less Sensitive Line (Wavelength Å)	Slit Å	Sensitivity *
Fe	3059.1	2	25
Cu	2165.1	2	6
Mn	4030.8	2	10
Zn	3075.9	7	4500
Pb	3683.5	7	25
Pb	2614.2	7	10

* Sensitivity - times less sensitive than most sensitive line

Standard sludge samples A and B from the Canada Centre for Inland Waters (CCIW) were analysed. Results obtained for Fe, Cu and Mn at the less sensitive and most sensitive lines are shown in Table 6. These means and standard deviations were computed on at least six replicate determinations. Results for lead and zinc are not shown because of gross problems which occurred, invalidating the use of the less sensitive lines.

TABLE 6. COMPARISON OF RESULTS FOR MOST SENSITIVE AND SELECTED LESS SENSITIVE ATOMIC ABSORPTION LINES

Element	Wavelength Å	A		B	
		$\bar{x}$	Sx	$\bar{x}$	Sx
Fe	2483.2	0.44	.03	6.8	0.4
%	3059.1	0.48	.01	6.4	0.1
Cu	3247.5	145	10	1180	100
ppm	2165.1	140	10	1130	20
Mn	2794.8	240	10	370	30
ppm	4030.8	270	10	400	20

These results show that better repeatability is obtained using the less sensitive lines. A comparison of the results with accepted values shows that the less sensitive lines give results in acceptable agreement.

4. APPLICABILITY OF HIGH TEMPERATURE COMMERCIALY AVAILABLE NON-FLAME ATOMIZERS

Graphite furnace, carbon rod and tantalum ribbon high temperature, non-flame atomizers are available (cost \$3000-\$8000) as attachments for atomic absorption equipment. Tremendous pressure has been exerted on atomic absorption users, suggesting that these devices are indispensable components of any atomic absorption setup.

The current literature contains many unproven statements to support the above contention. The most common of these are:

- 1) Limits of detection are several orders of magnitude lower using flameless devices.
- 2) Selective volatilization of matrix components before analyte (or vice versa) on a flameless atomizer is a generally applicable method of reducing interference problems.

If these contentions prove to be true for a wide range of applications, then most laboratories would find commercial flameless devices important accessories for atomic absorption equipment.

Some elements of interest in sludge are usually present in sub ppm amounts, e.g. Mo, Ag, Co, As, and Se. Others, e.g. Hg, Pb, Cd and Ni, suffer from serious matrix interference problems. It is essential, therefore, to critically evaluate available high temperature flameless atomizers for use in sludge analysis.

For the purposes of this study, a Perkin Elmer HGA 2000 Graphic furnace was used. At the time of this investigation, this device was found to be the most generally attractive of the commercial offerings.

4.1 Preparation of Sample Solutions

Samples were prepared for analysis in a manner reported earlier (22). The sample volume inserted into the furnace was generally 10 μ l. However, under some circumstances up to 50 μ l can be used.

4.2 Elements Chosen for Test

The elements chosen for experimental work were Mo, Co, Cd, Pb, Se and Ni. Experimentation with this range of elements, with widely differing chemical and physical behaviour, is an excellent test of the general applicability of the device.

At an early stage, work with selenium was abandoned because of the very poor signal to noise ratios obtained with even 10 ppm levels of this element. The most sensitive line for selenium is 1960 $\text{\AA}$ and work at this wavelength with a graphite furnace using hollow cathode lamps is unreasonable. Electrodeless discharge lamps with much improved signal intensity in this wavelength region are now available but require purchase of a separate power supply.

4.3 Experimental Conditions

Table 7 summarizes the instrumental parameters determined to be best for each element.

TABLE 7. INSTRUMENTAL PARAMETERS

	Mo	Cd	Co	Cu	Ni	Pb
λ Absorbing (nm)	313.3	228.9	240.9	324.8	232.0	217.0
λ^* Background (nm)	-	226.8	239.3	296.1	231.6	220.4
Spectral slit width (nm)	0.20	0.65	0.20	0.20	0.065	0.65
HGA temperature ($^{\circ}\text{C}$)						
Dry	100	125	125	125	125	125
Ash	1000	500	1100	1100	1100	750
Atomize	2700	1800	2500	2500	2500	2300
Time (s)						
Dry	60	30	30	30	30	30
Ash	40	60	60	60	60	60
Atomize	30	20	15	15	15	15

* The deuterium arc background corrector was also used.

4.4 Claim for Usefulness of Selective Volatilization

In theory, matrix problems (non-specific background absorption and chemical interference) can be suppressed by selectively volatilizing the interferent away from the analyte. Any interfering substances, e.g. Ni salts (analyte) and Ca salts (matrix), should be separable by using the fact that they volatilize at different temperatures. It has been asserted that, with high temperature, non-flame atomizers possessing continuously variable temperature control, selective volatilization is a practical tool for interference suppression.

A variety of matrix constituents in the sludges were tested with the elements of interest in a program of selective volatilization. Extensive experimentation demonstrated that, for the vast majority of major inorganic matrix substances, e.g. salts of Ca, Fe, Al, Mg, Na and K, selective volatilization did not separate the analyte and interferent. This was true even when other reagents were added to change the volatility characteristics of analyte or matrix. Many organic compounds in the sludges are readily volatilized prior to analyte atomization and, therefore, selective volatilization may be useful for organic samples low in inorganic salts.

Experience with the furnace showed that background problems, often present at low levels in flames, were greatly enhanced in the furnace. The deuterium arc automatic background corrector often failed to adequately correct for non-specific absorption because of the large magnitudes encountered.

4.5 Claims for Better Detection Limit

Only in the cases of Mo and Cd were definite advantages in detection limit obtained for the flameless device. Table 8 summarizes detection limits obtained in this study compared to flame.

4.6 Calibration Curve Linearity

In flame work, it is common to have linear working curves at up to 80% absorption. With the flameless device, curves were commonly linear up to only about 50 to 60% absorption.

TABLE 8. FLAME AND NON-FLAME DETECTION LIMITS* (ppb)

Element	Flame	Flameless
Cd	10	2
Co	10	30
Mo	1000	50
Pb	30	10
Ni	40	80

* 2 standard deviations above background

4.7 Conclusion

These tests suggest that, for most elements in sludge, the flame is still the atomizer of choice. In fact, it should be emphasized that, with complex inorganic matrix samples, like sludge, furnaces can give serious background, nonspecific absorption problems which are not evident in flame atomizers.

As indicated in the sections above, for Mo, As and Se, hot flameless devices do have a place in sludge analysis. In the case of As and Se, such a device can be simple, inexpensive and home-made. A definite advantage for a commercial unit is evident only for Mo analysis.

5. QUARTZ "T" TUBE FURNACE FOR METAL COMPOUNDS STUDY

A good deal of controversy exists in the literature over metal losses during drying and dry ashing of organic samples such as sludge. Low recoveries of Hg, Cd, Pb and Zn are commonly attributed to the volatility of these metals and their compounds.

Work conducted in this laboratory has demonstrated low recoveries of metals after drying and ashing at elevated temperatures. However, in a number of cases, some losses could be attributed to the trapping of metals in refractory compounds (silicates?) produced as a result of the heating. These compounds are not readily attacked by mixtures of HNO_3/HCl , $\text{HNO}_3/\text{H}_2\text{SO}_4$ or $\text{HNO}_3/\text{HClO}_4$ which are commonly used for dissolution of ashed samples.

A direct method of detecting metal volatility losses would be useful rather than assuming losses because of low recoveries.

Flameless atomic absorption, using electric furnaces and flame heated tubes, cups, etc., has been applied to the direct analysis of metals in a few organic sample types. By this procedure, solids are inserted directly into the atomizer and the metal of interest is volatilized from the matrix at temperatures above 2000°C .

It might seem possible to use this equipment to study metal volatility loss during drying and ashing. However, over the temperature range of interest ($100\text{--}600^\circ\text{C}$), metal compounds often volatilize and are not detected by atomic absorption because they are not atomized. In addition, the environment of a graphite furnace is highly reducing, a condition not necessarily existing in other high temperature sample treatments.

The following describes a "T" tube furnace, developed in the University of Toronto laboratory, which can be used to both volatilize and atomize many metals through the use of separate heated chambers. Metal losses due either to the production of atoms or compounds can, therefore, be investigated.

Because it is likely that a metal will exist in different forms in different sample types, the "T" tube system should provide a simple means of testing samples, routinely, for possible metal loss during ash-

ing and drying. Through the knowledge of the temperature at which the metals volatilized, it may be possible to identify metal compounds in sludge.

5.1 Description

Figure 1 is a diagram of the proposed "T" tube. The atomizer section of the unit is heated by a furnace kept at 800-900°C. Hydrogen gas is inserted only into the atomizer and a H_2 diffusion flame is allowed to burn at the atomizer tube ends. The separator section is run under varying temperature programs. The furnaces are constructed from Chromel C wire wound on a quartz tube and insulated with asbestos. Power is supplied to the furnace by separate variacs. Note that a gas chromatograph column also appears in the diagram. This will be discussed below.

Temperature in the separator section is monitored using a calibrated thermocouple in one channel of a dual channel recorder. The signal from the atomic absorption unit is monitored in the other channel of the recorder. Temperature can be varied in the separator section using manual control of the variac. Temperature is calibrated with salts of known melting point.

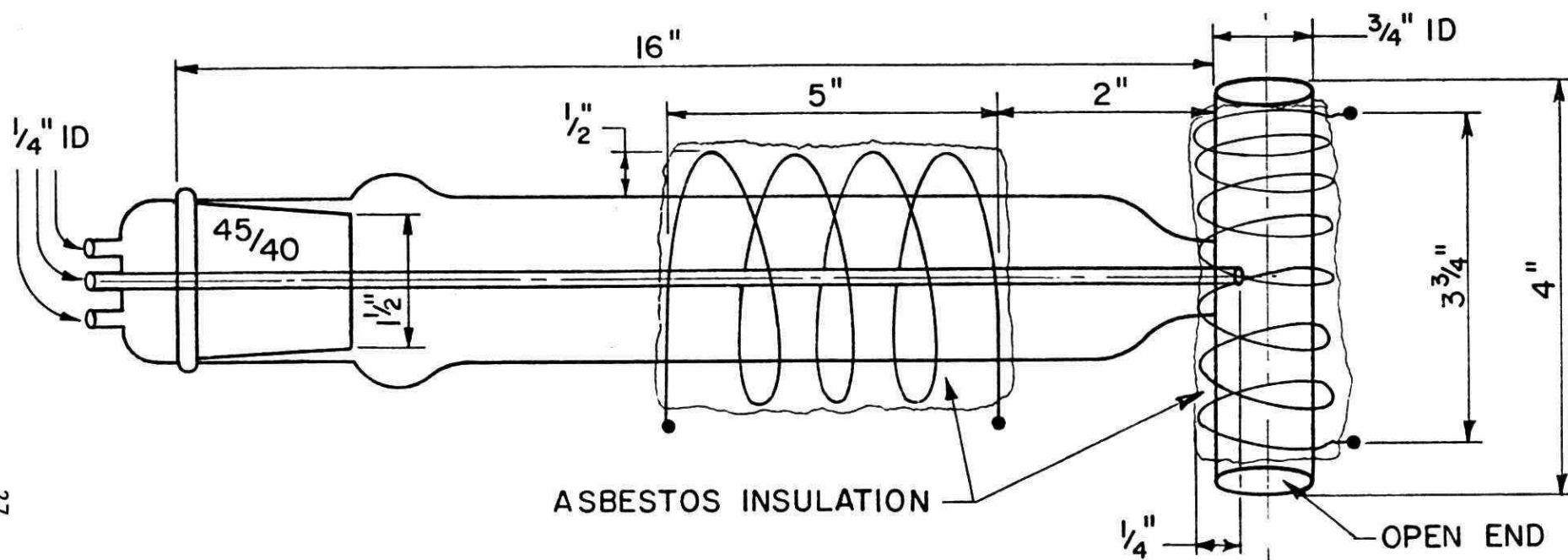
The system can be used with any purge gas desired. Work to date has used N_2 , Ar, H_2 and air. The gas flow rate must be studied and optimized for each application.

The equipment used in this study was a Perkin Elmer 305-B atomic absorption unit, a Sargent Welch DSRG dual pen recorder and a thermoelectric reference junction.

5.2 Temperature Profile Procedure

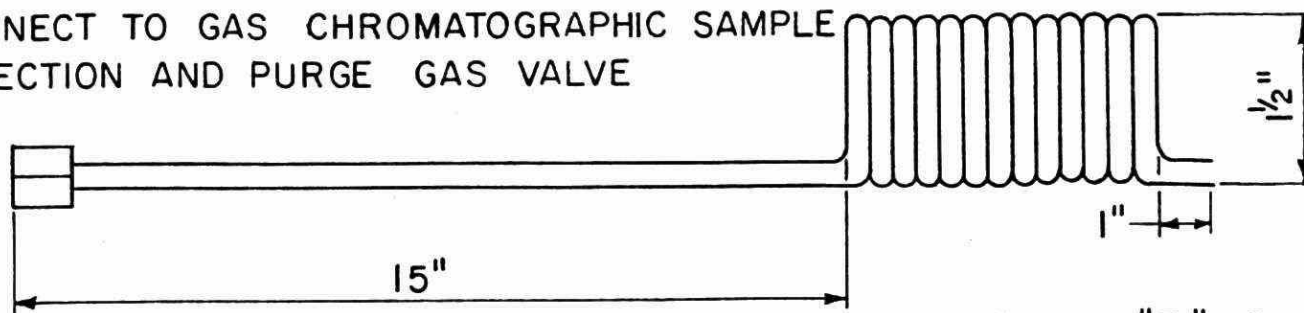
The absorption unit, including background corrector and the heater coil of the quartz atomizer, is turned on and allowed to warm up for 15 minutes. During the last 5 minutes the purge and hydrogen gases are turned on. The atomizer should be set at 900°C.

The ground glass joint is detached and the sample is inserted (can be wet or dry). The glass joint is replaced and the purge gas is allowed to flush out the system. The gases are turned on and stabilization is allowed for 5 minutes. The temperature pen is set on baseline. The signal pen is set to zero baseline (instrument is depressed to zero as well).



HELIX WOUND ALUMINIUM METAL
GAS CHROMATOGRAPHIC COLUMN

CONNECT TO GAS CHROMATOGRAPHIC SAMPLE
INJECTION AND PURGE GAS VALVE



QUARTZ "T" TUBE FURNACE

FIGURE 1.

Heating is begun slowly and the temperature is allowed to rise to the maximum desired. The temperature and atomic absorption signals are recorded.

5.3 Initial Results

Work to date has centred on mercury, cadmium, lead, arsenic and selenium. Greatest emphasis has been placed on mercury. It is not, at this stage, possible to draw firm conclusions. However, some trends of interest have been observed.

Results indicate that the mercury in the North Toronto, Newmarket and Point Edward sludges is lost, in large part, (>90%) over the temperature range 140 to 160°C. Figure 2 is a typical trace for mercury volatility from the North Toronto sludge. A loss of mercury at this temperature is consistent with mercury present in an inorganic form, possibly mercuric chloride.

To more readily define the form of mercury, a 5 ft helix wound, gas chromatographic column has been designed which will fit into the quartz "T" tube furnace (see Figure 1). In this way, advantage can be taken of the unique separational abilities of the gas chromatography and the high selectivity of atomic absorption spectroscopy. The design shown in Figure 1 has several advantages over previously proposed gas chromatographic/atomic absorption equipment. These include simplicity of design and interfacing, and much lower cost.

Early results for cadmium, lead and arsenic suggest that these elements, like mercury, are present largely in inorganic compounds. Work presently being done using chromatography and atomic absorption should allow more definite conclusions over the next year.

5.4 Comment on This Approach

The development of this quartz "T" tube separator/atomizer appears to be a very important step in the study of metals in sludge. It is likely that data obtained by this approach, coupled with studies done using selective extractants (e.g. DPTA, EDTA, acetates), will, in the near future, allow useful comments to be made on the potential for heavy metal uptake by plants.

MERCURY ABSORBANCE

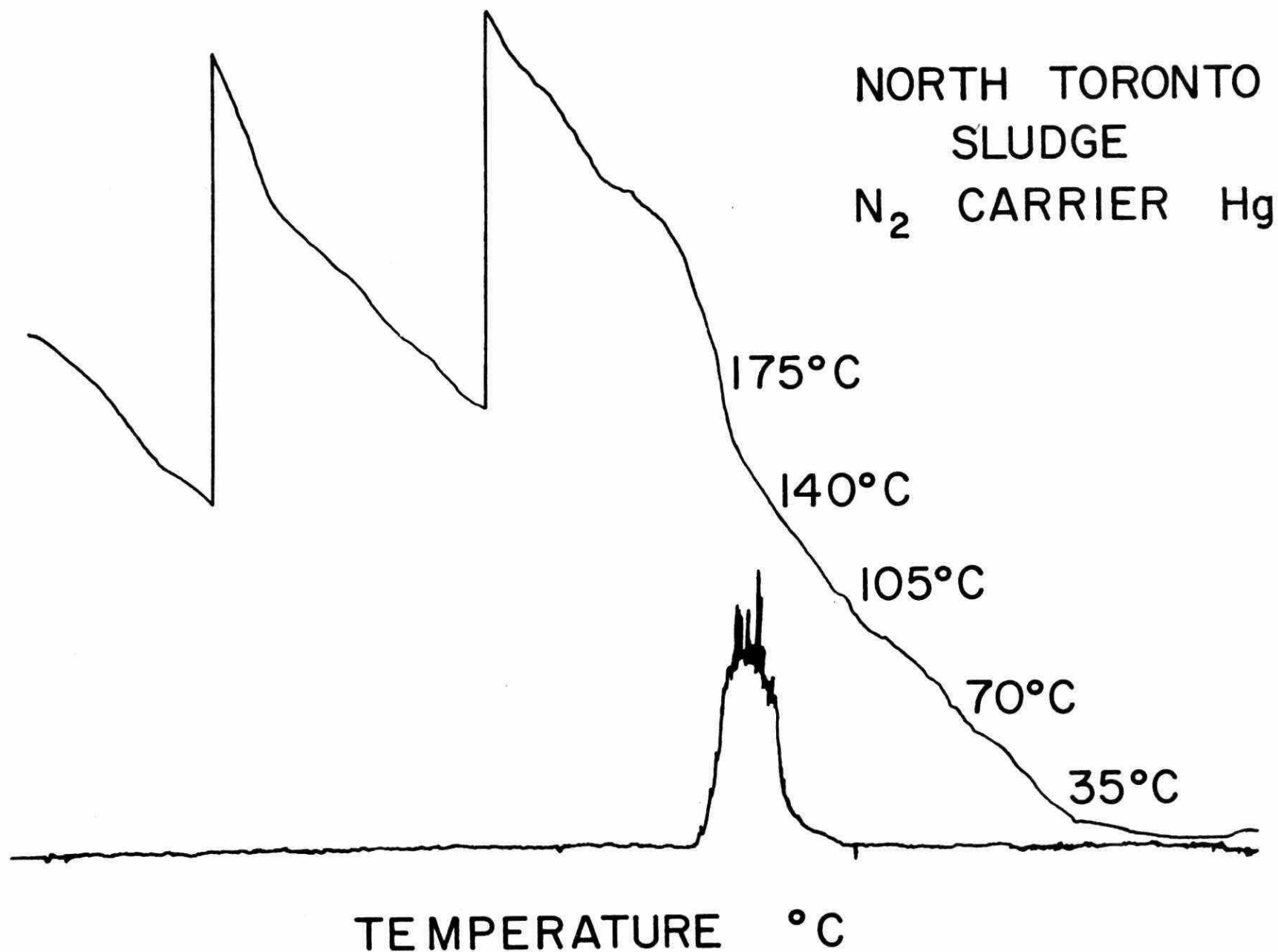


FIGURE 2. TRACE FOR MERCURY VOLATILITY IN NORTH TORONTO SLUDGE.

6. ANODIC STRIPPING

6.1 Introduction

Recent developments in electronic circuitry have resulted in inexpensive, easy to operate, electrochemical instruments for polarography and anodic stripping voltametry. Instead of being restricted to D.C. operation, the new instruments offer a differential pulse mode. This innovation greatly simplifies the output charts and gives much improved detection limits.

Previous experience with D.C. instruments has shown that polarography and anodic stripping cannot be used for analysis of complex sample solutions such as would result from dissolving sewage sludges. However, these conclusions should be re-evaluated using new equipment incorporating the recent developments mentioned above.

Of the two techniques, anodic stripping is the most attractive. By this method, metals are removed from the sample solution into a mercury drop (amalgamate) during a reduction stage. The mercury drop is then made the anode and the metals are stripped from a simple mercury matrix.

This study, to date, has emphasized anodic stripping, using the following procedure as a beginning point. Modifications to this procedure are being made continually and will be reported when they have been properly tested.

6.2 Equipment

A Princeton Applied Research (PAR) Model 174 and a Houston Instruments X-Y Recorder Model 2000 were used.

6.3 Procedure

Instrument Settings:

Initial Potential, - 1.1 V (initial button depressed)

Scan rate, 5 mv/sec.

Direction, +

Range, 1.5 V

Modulation Amplitude, 25 mV

Mode, differential pulse

Current Range, 0.5 to 5 μ A

Drop time, 0.5 sec.

Display Direction, -

Recorder Settings:

X axis, 100 mV

Y axis, 1 V

The sample is outgassed for 10 minutes using N_2 (see Section 6.5). A magnetic stirrer adjusted to a very low speed is used. A hanging mercury drop is formed, using 6 units on the micrometer. After 30 seconds, the gas bubbler stop cock is turned to the cell flushing position (stops bubbling). The selector switch is turned to the external cell position and electrolysis is allowed to proceed for 60 seconds. The stirrer is then turned off. After 15 seconds, the scan button is depressed and tracing is recorded (see Section 6.5). A new Hg drop is used for each run.

Calibration is done by the standard additions method, using single element standard solutions prepared in acetate buffer as per the sample.

6.4 Sample Solutions

The pH of the sample is adjusted to about 2 before adding the buffer. When ready for analysis, 1.0 ml acetate buffer (see Section 6.5) and 0.165 ml 20% NaOH are added.

6.5 Notes

- 1) Outgassing N_2 should be passed through a vanadous chloride scrubber and then through a solution of the buffer to saturate the N_2 gas with volatile components prior to passage through the sample solution.
- 2) Varying current range settings are needed, e.g. 5 μA for Zn, 0.5 μA for Cd and Pb, 2 μA for Cu.
- 3) Acetate buffer is 570 ml glacial acetic acid and 52 g of sodium acetate diluted to 1 litre with water.

6.6 Results

The above procedure can be used for Zn, Cd, Pb and Cu. Other elements require use of different complexing agents, solvents, etc. and cannot easily be done without extensive modifications at this stage. Work in this regard is proceeding.

Good results have not been obtained for sludge samples; however, as a step in this direction, the aqueous fraction of sewage has been subjected to an extensive study. Results obtained, compared with atomic absorption, are presented in Table 9. A number of standard reference samples, not as complex as sewage sludge, were also analysed as another step toward evaluating the potential of anodic stripping for sludge analysis.

TABLE 9. RESULTS OF METAL ANALYSIS BY ANODIC STRIPPING (ppb)

Sample	Zn	Cd	Pb	Cu
Sewage Liquid (a)	43* (60)	0.8 (0.5)	5 (2)	16 (21)
(b)	48 (70)	-	8 (6)	13 (20)
(c)	28 (34)	0.4 (0.3)	4 (1)	10 (14)
(d)	32 (34)	5 (0.3)	6 (2)	12 (12)
(e)	20 (23)	-	6 (3)	25 (27)
NBS, Orchard Leaves #1571	38** (25)	11 (0.1)	52 (45)	15 (12)
NBS, Liver #1577	88 (130)	6 (0.3)	20 (0.3)	125 (173)

* AAS results

** NBS provisional values

6.7 Discussion

Results to date indicate that anodic stripping gives results which are not comparable to atomic absorption results or National Bureau of Standards values. Results for sewage liquids were much better than for solids which had been dissolved. In no case, however, were satisfactory results obtained by anodic stripping.

Results for polarographic analysis were worse and, therefore, are not included.

Recent work suggests that anodic stripping may, with further developmental work, prove applicable to sewage liquids for the elements Cu, Zn, Pb and Cd. Analysis for other elements would require extensive manipulation of solution composition, which, although time consuming, should expand the list that can be done.

At present, it appears that anodic stripping cannot be used as a tool for sludge analysis. Atomic absorption is more suitable for a wide variety of elements.

7. ANALYSIS OF AVAILABLE CHEMICAL SLUDGES

Fortnightly sludge samples were obtained from sewage treatment plants which agreed to cooperate with this study. Only chemical treatment sludges were of interest.

7.1 Method of Collection

A quart size grab sample was obtained daily from the digester and stored in a large container. At the end of a two week period the sample in the large container was homogenized and a pint sample removed for analysis.

7.2 Laboratory Control

A CCIW standard sludge was analysed with each sludge batch. Results were in acceptable agreement with values reported by this laboratory in previous reports (22). Results are tabulated in Table 10.

TABLE 10. SLUDGE METAL RESULTS (Dried weight)

		Zn	Fe	Cu	Mn	Cr	Ni	Cd	Pb	Al	Hg	As	Solids
		%	%	%	ppm	ppm	ppm	ppm	%	%	ppm	ppm	%
1 July 29	A	0.25	7.5	0.12	375	900	250	18	0.11	0.70	7	1	3.2
	B	0.31	5.3	0.12	350	940	240	29	0.13	0.72	10	1	5.0
	C	0.25	4.4	0.14	340	850	250	30	0.11	0.65	6	1	3.7
	D	0.21	5.0	0.16	400	830	250	23	0.11	0.61	8	0.6	3.8
	*E	0.16	4.4	0.09	200	700	82	15	0.13	0.47	5	0.6	7.3
	*F	0.15	4.0	0.09	190	700	77	14	0.12	0.44	5	0.6	7.4
	G	0.18	4.3	0.14	200	695	170	21	0.10	0.44	5	0.8	2.9
	H	0.17	4.7	0.21	220	730	200	22	0.13	0.44	6	0.8	3.0
	I	0.17	4.8	0.23	300	730	130	18	0.10	0.44	6	0.6	3.4
	J	0.23	3.3	0.21	310	625	280	23	0.09	0.43	7	0.6	2.7
	K	0.21	3.7	0.16	300	550	240	19	0.09	0.44	5	1	3.0
2 July 22		%	%	ppm	%	ppm	ppm	ppm	%	%	ppm	ppm	%
	A	0.15	5.8	350	0.40	250	35	37	0.17	0.50	5	1	3.5
	B	0.17	6.5	375	0.40	280	27	35	0.16	0.47	6	1	3.0
	C	0.19	5.5	360	0.64	280	28	47	0.13	0.34	4	1	3.7
3 Aug. 26		%	%	ppm	ppm	ppm	ppm	ppm	ppm	%	ppm	ppm	%
	*A	0.18	1.0	950	310	880	180	10	490	4.0	9	0.6	4.6
	*B	0.28	5.8	1150	400	860	220	24	1000	0.65	7	0.6	2.7
		%	%	%	ppm	ppm	ppm	ppm	ppm	%	ppm	ppm	%
4 Aug. 15	A	0.10	5.3	0.11	300	70	15	7	440	0.31	9	0.5	3.1
	B	0.10	8.3	0.10	425	75	12	7	375	0.25	13	0.6	4.1
	C	0.08	8.4	0.07	380	88	15	5	310	0.20	8	0.6	3.6
	D	0.08	6.3	0.09	360	65	13	6	250	0.21	7	-	3.3

1 Brantford

2 Woodstock

3 Barrie

4 London

* Samples with similar dates

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